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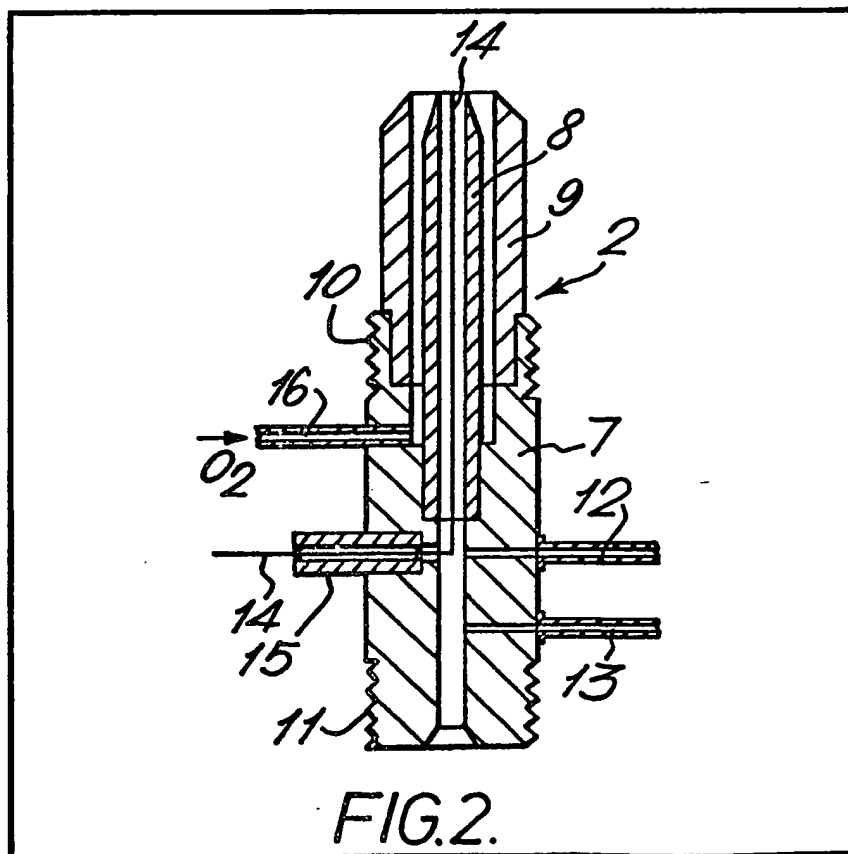
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(54) Flame ionisation detector and method of use thereof

(57) A flame ionisation detector comprises a burner 2 having two coaxial tubes 8 and 9, one for conveying to the flame a mixture of a first gas, eg. H₂, and the sample to be detected and the other for conveying to said flame a second gas, eg. O₂, which combusts with said first gas. The coaxial tubes 8, 9 can be of metal, eg. stainless steel, or ceramic, eg. alumina, magnesia, silica or zirconia. A polarising electrode 14 may be disposed in the burner 2, eg. formed as a wire 14 in inner tube 8, as shown, of Pt, W or stainless steel or as a metallic coating on a wall of one of the tubes 8, 9 formed by pyrolysis of tungsten or titanium halide. Preferably the sample is entrained in an inert carrier gas, eg. N₂ or He. The

detector exhibits reduced levels of noise and standing current when supplied with oxygen and hydrogen and the response of the detector in a gas chromatograph can be manipulated by varying the flow rates and proportions of the gases fed to the flame, whereby it is made to be responsive to the molar amount or the weight of an organic eluting solute or to be selective in favour of organic compounds containing elements other than carbon and hydrogen.



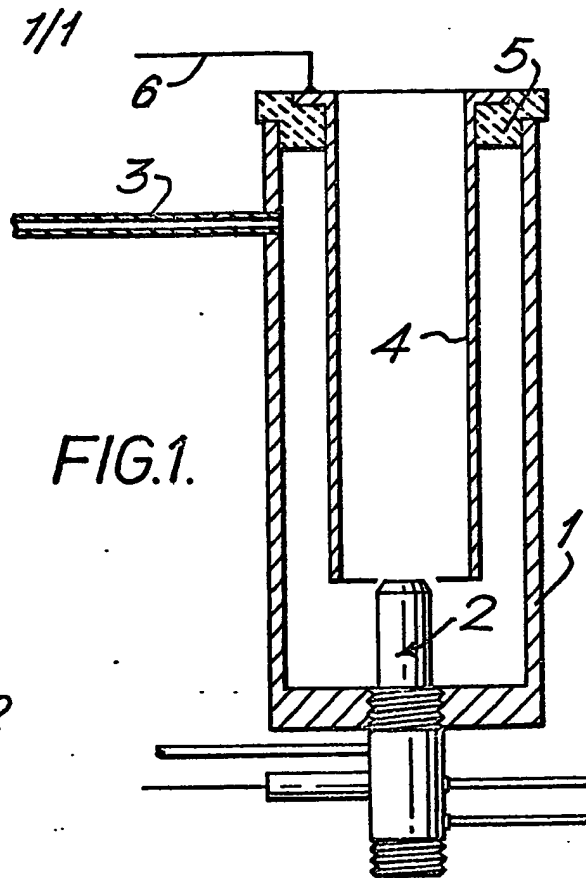


FIG. 1.

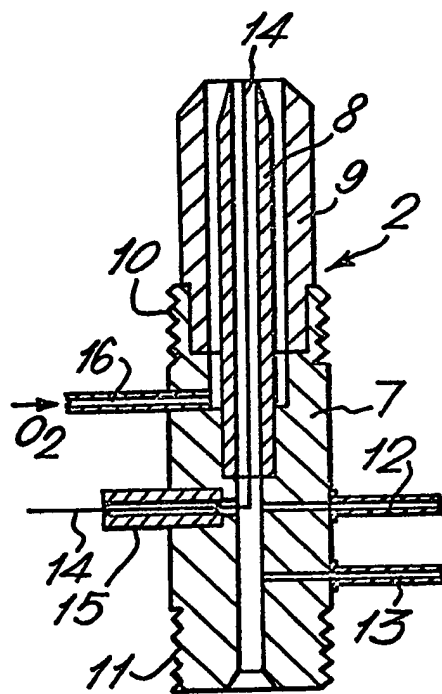


FIG. 2.

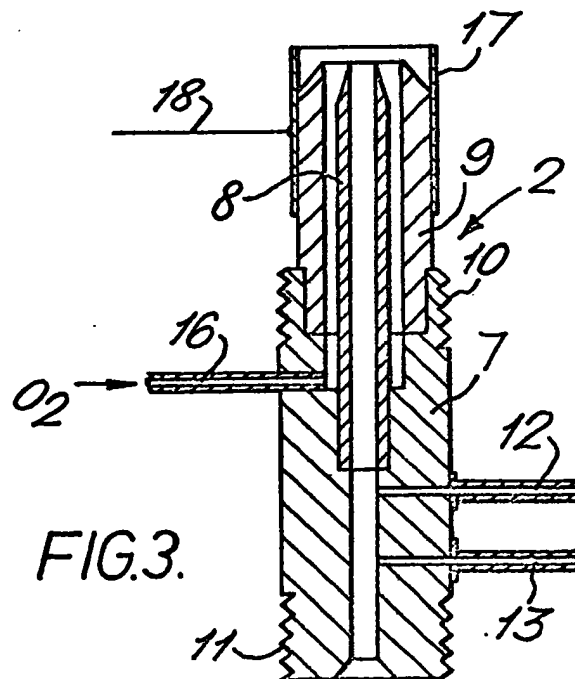


FIG. 3.

SPECIFICATION

Flame ionisation detector and method of use thereof

- 5 This invention concerns an improved flame ionisation detector (hereinafter abbreviated to FID) 5
for use with a gas chromatograph.

In a gas chromatograph, the detector is the device which indicates when the carrier gas contains a component derived from the sample being analysed. The detector is required to be extremely sensitive to small amounts of a wide range of organic compounds, and to give an
10 output related to the amount of such compounds in the carrier gas. The FID is probably the most 10
widely used sensitive detector because of its relative ease of construction, robustness, linear
response and wide dynamic range. In spite of its advantages, the FID has the serious drawback
that the presence of elements other than carbon and hydrogen in the eluting solutes leads to a
reduction in response. This unfortunate property necessitates calibration of the detector for each
15 species under investigation when quantitative studies are to be performed. 15

We have described how the response of the FID is markedly changed when the device is operated in an atmosphere of pure oxygen, especially when the ratio of hydrogen to oxygen exceeds that normally employed in conventional FID operations (J. Chromatog. 150 (1978) 533-536 and 329-338; J. Chromatog. 158 (1978) 139-151; also British Patent Application
20 34961/77). The aforesaid references disclose that, under certain conditions described therein, 20
the FID gives an equimolar response, i.e. the response in coulombs per mole is substantially
constant for organic compounds of different structure. For example, a given mol fraction of
benzene, monochlorobenzene, dichlorobenzene or trichlorobenzene will give the same response,
and alkanols give practically the same response as the corresponding alkanes.

25 As the proportion of hydrogen is increased further, the response becomes dependant on the 25
weight of eluting solutes, i.e. the response per gram of solute is practically constant, at least for
the solutes investigated. In this condition, one can determine directly the percentage composition
of an unknown mixture without even knowing the nature of the components. Furthermore,
by comparison with the first-mentioned mode of operation, one can determine the molecular
30 weight of a solute if a known compound can serve as a standard. 30

Thirdly, if the proportion of hydrogen is increased still further, the response of the FID again becomes selective. However, under these conditions selectivity is practically the opposite of that
seen under conventional operating conditions. Under conditions of great hydrogen richness
(compared to normal FID operation), the response to C and H is largely suppressed, and the
35 response to heterogeneous atoms, e.g. halogens, sulphur, nitrogen or phosphorus is enhanced. 35
Under these conditions one can, for instance, observe the presence of traces of halogenated
benzenes in the presence of an excess of benzene.

In the aforesaid literature references a conventional FID was used in a novel manner to obtain novel and valuable modes of response. However under these conditions the conventional FID
40 exhibits certain drawbacks. Most notably, the noise level is increased, especially at higher gas 40
flow rates. The increase may amount, for instance, to one or two orders of magnitude, and
places a limit on the sensitivity of the device. Furthermore the standing current is greatly
increased. At high gas flow rates the increase may be as much as four orders of magnitude
compared with normal FID operation using air. This high standing current causes difficulty in
45 maintaining stable operation and leads to drifting of the base line and spurious responses near 45
the detection limit. These problems are particularly prevalent in the selective mode of operation.
Although valuable results can be obtained using an FID of conventional construction, it would
be desirable to improve the operating characteristics of the FID when used with oxygen.

One aspect of our invention provides a flame ionisation detector wherein the burner has two
50 coaxial tubes, one for conveying to the flame a mixture of a first gas and the sample to be 50
detected and the other for conveying to said flame a second gas which combusts with said first
gas.

The concentric construction of the burner reduces the temperature of the burner tip and hence greatly reduces thermionic emission, which is responsible for much of the electrical noise
55 detected by the FID when running on pure oxygen. In this mode of operation the flame 55
temperature is much higher than under conventional operating conditions. Thermionic emission
is exponentially dependant on temperature and hence a modest change in burner temperature
will markedly alter the noise level.

Although the said coaxial tubes may be made of a suitable heat-resistant metal, such as
60 stainless steel, it may be preferred to make at least the portions of the tubes adjacent the flame 60
of a refractory ceramic material. This provides a further reduction in thermionic emission. A very
satisfactory ceramic material is alumina; other materials include magnesia, silica and zirconia.

Preferably the annulus between the inner and outer burner tubes has a portion of increased area adjacent its open end, produced e.g. by a bevel or chamfer on the outer edge of the inner
65 tube and/or on the inner edge of the outer tube, or less desirably by flaring the end of the outer 65

tube or by providing stepped portions near the end of one or both burner tubes. This feature reduces gas velocity immediately adjacent the flame and enhances flame stability. If the inner edge of the outer tube is not bevelled, the outer edge may be provided with a bevel or chamfer.

- When one or both of the burner tubes is of metal, it may also serve as the polarising
- 5 electrode. In the preferred construction using ceramic tubes a separate polarising electrode is 5 necessary. This may for example be a metal annulus surrounding the outer burner tube adjacent the flame but preferably not in contact therewith. However, in this position the polarising electrode tends to become hot enough to exhibit thermionic emission. According to a novel and valuable feature of our invention the polarising electrode, e.g. a wire, is situated in the inner
- 10 tube of the burner assembly. In this position it is efficiently cooled by a gas stream. Moreover 10 the wire electrode may terminate a short distance, e.g. 0.5 to 3mm, from the end of the inner burner tube. We have found that an electrode so situated still gives efficient polarisation and, being well clear of the flame, remains very cool in use. The polarising electrode can be of any suitable metal, e.g. platinum, tungsten or stainless steel.
- 15 The polarising electrode may also be formed by a conductive e.g. metallic, coating on the 15 inner or outer walls of the inner burner tube or on the inner wall of the outer tube. Such a coating may e.g. be formed by pyrolysis of a tungsten or titanium halide. The coating should preferably terminate a short distance from the end of the tube, so as to remain cool in use.
- The two burner tubes are generally mounted on a manifold having inlets for the two gases.
- 20 Conventionally there are inlets for the combustible gas, for the gas supporting combustion, and 20 for the column effluent which is mixed with one or other of the gases before being conveyed to the flame. The column effluent will comprise a carrier gas as well as the solute to be detected. It is useful to provide the manifold with a further inlet for make-up carrier gas to enable the volume of carrier gas to be adjusted to suit the desired mode of FID operation without altering
- 25 the parameters of the column. 25
- According to another feature of our invention, the FID includes means for connection to a supply of cooling gas to cool the ion-collecting electrode. Any inert gas such as nitrogen or helium can be used to reduce the temperature of the collector electrode and thus reduce the possibility of thermionic emission. In conventional FID operation the flame is supplied with an
- 30 excess of air which serves to cool the device as well as supporting combustion of the flame. 30 When an FID is supplied with pure oxygen, not only is the flame much hotter but the total gas flow through the device is significantly reduced. Thus the provision of a supply of inert cooling gas can be regarded as replacing the nitrogen component in the air supplied during conventional FID operation.
- 35 The first and second gases which combust together in the flame of the FID will generally be 35 oxygen and hydrogen, but other gases may be used in the FID of this invention. For example, the oxidising gas may be nitrous oxide; the reducing gas could be ammonia. These are both endothermic compounds which burn with a very hot flame.
- In use of the FID the oxygen or other oxidising gas is generally fed to the annulus between
- 40 the inner and outer burner tubes. The inner tube, carrying hydrogen, may e.g. have a bore in 40 the range 0.012–0.040 in (0.3–1.0 mm). Irrespective of the flow rate, if the velocity of combustible gas is too high due to the use of a tube of too small bore, the response of the FID is seriously compromised.
- However, it is also possible to supply oxygen through the inner tube, in which case a
- 45 somewhat smaller bore may be desirable. The sample will generally be mixed with the 45 hydrogen, but may instead be mixed with the oxygen or other oxidising gas.
- Apart from improved noise level and standing current, the FID of our invention is easy to handle in the modes of operation described in the aforementioned literature references. In particular the conditions for the three modes of operation are quite easily located. By and large,
- 50 in selecting the gas flow rates to produce any required response, the same principles apply as 50 disclosed in the aforementioned literature references although ratios and absolute values will vary somewhat depending on the geometry of the particular device. Some preliminary tests are needed to set up a particular FID for optimum operation in one of the three possible modes, but these tests are neither difficult nor lengthy.
- 55 The following general discussion together with the disclosure in the literature references 55 referred to above will enable those skilled in the art of gas chromatography to obtain the benefit of our invention after a minimum of experiment to determine the optimum operating conditions.
- In general, the following relationships have been observed using nitrogen as the carrier gas:
- (a) At fixed oxygen and nitrogen flow rates, the FID response varies with the hydrogen flow
- 60 rate. At lower flows the response is molar, at a defined higher flow it is weight responsive and 60 above this level it becomes increasingly selective,
- (b) At fixed nitrogen flow rates, the absolute response of the FID increases with increasing combined oxygen/hydrogen flow rate. This effect diminishes as the nitrogen flow rate increases.
- (c) At a fixed hydrogen/nitrogen ratio, the effect of increasing oxygen flow is mainly to
- 65 increase the absolute response of the FID without much affecting the positions of equimolar or 65

equal weight responses.

Considering now the molar response mode, the flow rates are in general not very critical. For example, a molar response may be obtainable at least over the range of H_2/O_2 flow rates of 1:3 to 1:1, more preferably in the range 1:2.5 to 1:1, by suitable selection of the flow rate of the nitrogen carrier gas. Ratios of flow rates herein are on a volume bases. As the ratio of H_2/O_2 is increased, the flow of carrier gas may also require to be increased to maintain molar response.

We have mainly used nitrogen as the carrier gas, but other inert carrier gases such as helium can be used with appropriate adjustment of operating conditions; argon has not given good results in the molar response mode. In the molar response mode the use of an inert carrier gas is very desirable. Without an inert carrier gas (i.e. using hydrogen as the carrier), the response only approximates to molar at very low hydrogen flow rates.

The ability to obtain a molar response over a significant range of carrier gas flow rates enables the FID to be matched to the conditions for good separation on a variety of packed columns. For capillary columns provision of make-up carrier gas may be necessary to achieve the requisite balance of flow rates for molar response.

Under all conditions of use of the FID according to our invention, it is usual to follow the conventional practice of maintaining the FID at an elevated temperature, e.g. in the range 100–350°C, but low enough to avoid significant thermionic emission.

The weight response mode of operation requires more critical selection of parameters. When an inert carrier gas such as nitrogen is used, there is generally, for each combination of oxygen and hydrogen flow rates, only one nitrogen flow rate or at most a narrow range of flow rates which will give equivalent weight response. At the lower limit of hydrogen flow there may be a unique combination of N_2 and O_2 flow rates to give the required response. Intermediate values of hydrogen flow give the choice of a variety of O_2/N_2 ratios, but at higher rates of H_2 flow the choice again becomes limited. In general, increasing the N_2 flow requires a reduction in O_2 flow.

To operate the detector in the weight response mode the chromatographic conditions for satisfactory separation should first be determined. Having fixed the flow rate of carrier gas, a combination of O_2 and H_2 rates giving the desired mode of operation may then be selected by reference to the characteristics of the FID as previously determined. The conditions for the weight response mode may also be affected by the nature of any heterogeneous atoms in the solutes. When a variety of heterogeneous atoms is present in different solutes, it may not be possible to find conditions giving an accurate weight response for all solutes in the mixture.

For the weight response mode of operation there are advantages in using hydrogen as the carrier gas where this is chemically feasible. For a given hydrogen flow rate there may be a significant range of oxygen flow rates giving equivalent weight response. For use with low flow-rate capillary columns one can add make-up hydrogen to the column effluent to increase the H_2 flow rate to a value adequate for good FID operation.

In both the molar and weight response modes, the absolute response of the FID is enhanced if the O_2 flow rate is high.

Finally, under hydrogen-rich conditions the response to carbon is progressively depressed. This effect is most apparent when using volume ratios of H_2/O_2 of at least 1.25:1, preferably at least 1.5:1 and is even more marked at a ratio of 2:1. The effect is at a maximum with low proportions of inert carrier gas (e.g. nitrogen). Thus the use of hydrogen as the carrier gas may be advantageous in this mode of operation. The optimum rate of flow of a nitrogen carrier can readily be found by experiment but is often in the range 15–25% of the combined O_2 and H_2 rates. Not only is the FID in this mode selective in favour of heterogeneous atoms but the absolute response to the heterogeneous element is higher than the response to carbon in the conventional mode of operation. The absolute response to, e.g., 1,2,4-trichlorobenzene may be nearly 300 times that of a conventional FID. Previously it has been customary to employ special selective detectors for each heterogeneous element of interest e.g. sulphur, phosphorus, nitrogen or halogen. It is now possible to use an FID with good efficiency for the same purpose. The carbon response is not completely suppressed but it can be made very small. For example, the response to benzene can be less than 1% of the response to 1,2,4-trichlorobenzene. An advantage of the FID used in this mode over an electron capture detector is that it does not respond appreciably to aromatic nuclei while responding strongly to electron capturing heterogeneous atoms such as halogen and sulphur.

Thus a further aspect of our invention is a method of operating a gas chromatograph having a flame ionisation detector according to the invention wherein said flame ionisation detector is operated under conditions such that the response of said detector is

- (a) substantially proportional to the molar amount of an eluting organic solute;
- (b) substantially proportional to the weight of an eluting organic solute; or
- (c) selective in favour of organic compounds containing elements other than carbon and hydrogen;

and using said chromatograph to separate a mixture of organic compounds.

Two embodiments of our invention are illustrated diagrammatically and by way of example

only in the accompanying drawings, in which:—

Figure 1 is a cross-section through an FID according to our invention;

Figure 2 is an enlarged view of the burner assembly of the FID of Fig. 1; and

Figure 3 is a cross-section through an alternative burner assembly using a different disposition of polarising electrode.

Referring now to Fig. 1, the FID comprises a generally cup-shaped housing 1 of stainless steel, in the base of which is centrally disposed the burner assembly 2. Near its upper end the housing is provided with an inlet 3 for cooling gas, generally nitrogen. The cylindrical collector electrode 4 of stainless steel is coaxially mounted in the housing 1 and insulated therefrom by the insulating bush 5. The lead 6 is connected to the input of an amplifier.

Referring now to Fig. 2, the burner assembly 2 comprises a manifold block 7 into which are mounted coaxial inner and outer burner tubes 8 and 9 respectively. The inner tube 8 has an outside diameter of 2 mm and a bore of 0.5 mm while the outer tube 9 has an outside diameter of 4.2 mm and a bore of about 2.5 mm. Both tubes are in fused alumina (available from Thermal Syndicate), and are mounted in the manifold block with ceramic cement. The top end of the tube 8 is bevelled on its outer edge, to an apex of about 30°, thus increasing the area of the annulus between the tubes at this point and correspondingly reducing gas velocity. The tube 9 is also bevelled on its outer edge.

The manifold block 7 has a threaded portion 10 by which it can be mounted into the housing 1. At its base there is a threaded union 11 for connection to the outlet of a chromatography column. Inlet 12 for hydrogen and inlet 13 for make-up gas both communicate with tube 8, and gases fed through these inlets are thoroughly blended with the column effluent before reaching the top of the burner.

The polarising electrode 14 comprises a piece of stainless steel wire terminating at the top of the burner assembly and leaving the manifold block through the insulating sleeve 15, of alumina, into which it is sealed by ceramic cement. The annulus between the inner and outer burner tubes communicates with oxygen inlet 16.

In the embodiment of Fig. 3 the wire polarising electrode 14 is replaced by the stainless steel collar 17 having an internal diameter of 4.45 mm and cemented in place around the top of the outer tube 9. A lead 18 is, in use of the device, connected to a source of polarising voltage.

The following Table shows the improvement in noise and standing current seen in the FID of our invention when operated with oxygen and hydrogen, compared to a conventional FID operating in the same mode. The heading "O₂-H₂ FID" designates a standard Pye Unicam Series 104 FID, (available from Pye Unicam Ltd, Cambridge, England) while the designation "O₂-H₂ CB" indicates the embodiment of Figs. 1 and 2 just described, comprising a coaxial burner assembly with the difference that the burner tubes were made of stainless steel.

The operating conditions were as follows: column temperature, 116°; detector temperature 300°; nitrogen carrier gas flow rate 40.8 ml min⁻¹. For further comparison, the standing current and noise level of the conventional FID (Pye Unicam 104) operating with hydrogen and air are also tabulated.

TABLE 1

Flow-rate (ml min ⁻¹)		Standing Current (A)		Noise (A)	
Hydrogen	Oxygen	O ₂ -H ₂ FID	O ₂ -H ₂ CB	O ₂ -H ₂ FID	O ₂ -H ₂ CB
40	40	4.5.10 ⁻¹⁰	2.7.10 ⁻¹¹	1.5.10 ⁻¹³	8.0.10 ⁻¹⁴
60	60	6.2.10 ⁻⁹	1.8.10 ⁻¹¹	1.6.10 ⁻¹²	8.0.10 ⁻¹⁴
80	80	1.5.10 ⁻⁸	3.0.10 ⁻¹⁰	—*	8.0.10 ⁻¹³
125	125	1.8.10 ⁻⁷	5.2.10 ⁻⁹	—*	1.0.10 ⁻¹²
60	125	8.5.10 ⁻¹¹	1.1.10 ⁻¹⁴	4.0.10 ⁻¹¹	3.0.10 ⁻¹⁴
<i>Conventional FID</i>					
Hydrogen	Air				
50	500	1.4.10 ⁻¹¹		4.0.10 ⁻¹⁴	

*It was impossible to obtain a noise level at these flow-rates because the standing current was so high.

It will be seen that the FID of this invention exhibits a standing current one or two orders of magnitude lower than the O₂-H₂ FID and a much reduced noise level. These parameters are comparable with those for a conventional FID operated with air.

The following results indicate the way in which the response of an FID according to Figs. 1 and 2 herein can be manipulated by alteration of the flow rates of oxygen, hydrogen and

nitrogen to produce as desired a molar response, a weight response or a selective response in which the response to carbon is largely suppressed and the response to halogen is greatly enhanced. The test mixture contained benzene, chlorobenzene, 1,3-dichlorobenzene and 1,2,4-trichlorobenzene (B,MCB, 1,3-DCB and 1,2,4-TCB respectively) in the stated weight and molar percentages. A polarising voltage of -170V was applied to the central polarising electrode.

5 It is evident from the results in Table 2 that H_2 , O_2 , N_2 flow rates of 40, 80 and 40 ml min^{-1} respectively gave a close approximation to molar response; at 37.5, 85.5 and 5 ml min^{-1} a weight response characteristic was seen, while at 75, 37.5 and 0 ml min^{-1} the chlorinated solutes gave a selectively enhanced response. Except for benzene in the selective mode, all tests
10 showed a significantly higher absolute response than the conventional FID (Pye Unicam Series 104) operated with air. As may be seen from the small standard deviation values, the FID of this
invention was stable in operation and gave reproducible results in all modes of operation.

TABLE 2

Gas Flow Rates			Test Results		Test Solutes			
ml min ⁻¹				B	MCB	1,3-DCB	1,2,4-TCB	
H ₂	O ₂	N ₂	%wt %mole	15.20 25.29	20.97 24.21	28.59 25.27	35.24 25.22	
40	80	40	Observed % Composition	24.9	25.62	25.30	24.18	
			Standard Deviation	0.470	0.510	0.362	0.278	
			Absolute Response	4.19 × 10 ⁻²	3.11 × 10 ⁻²	2.25 × 10 ⁻²	1.78 × 10 ⁻²	
			Absolute Response	3.27	3.50	3.31	3.23	
37.5	85.5	5	Observed % Composition	14.98	22.80	28.24	34.18	
			Standard Deviation	0.481	0.416	0.355	0.738	
			Absolute Response	3.32 × 10 ⁻²	3.63 × 10 ⁻²	3.25 × 10 ⁻²	3.23 × 10 ⁻²	
			Absolute Response	2.59	4.08	4.82	5.86	
75	37.5	0	Observed % Composition	3.08	18.20	32.92	45.79	
			Standard Deviation	0.081	0.105	0.208	0.035	
			Absolute Response	1.25 × 10 ⁻²	5.32 × 10 ⁻²	7.06 × 10 ⁻²	7.97 × 10 ⁻²	
			Absolute Response	0.98	6.00	10.38	14.46	
H ₂	Air	N ₂	Normal FID Response					
			Observed % Composition	21.65	24.05	26.71	27.58	
			Standard Deviation	0.068	0.249	0.568	0.583	
			Absolute Response	1.75 × 10 ⁻²	1.41 × 10 ⁻²	1.15 × 10 ⁻²	0.96 × 10 ⁻²	
50	500	50	Absolute Response	1.36	1.59	1.69	1.74	

CLAIMS

1. A flame ionisation detector wherein the burner has two coaxial tubes, one for conveying to the flame a mixture of a first gas and the sample to be detected and the other for conveying to said flame a second gas which combusts with said first gas.
- 5 2. A flame ionisation detector according to claim 1 wherein the annulus between the inner and outer burner tubes has a portion of increased area adjacent its open end. 5
3. A flame ionisation detector according to claim 2 wherein a bevel or chamfer is formed on the outer edge of the inner burner tube and/or on the inner edge of the outer burner tube.
4. A flame ionisation detector according to any of claims 1-3 wherein at least the portions 10 of the burner tubes adjacent the flame are formed of a refractory ceramic material. 10
5. A flame ionisation detector according to any of claims 1-4 wherein the polarising electrode is situated in the inner tube of the burner assembly.
6. A flame ionisation detector according to claim 5 wherein the polarising electrode comprises a wire which terminates 0.5 to 3mm from the end of the inner burner tube.
- 15 7. A flame ionisation detector according to claim 4 wherein the polarising electrode is formed by a conductive coating on the inner or outer wall of the inner burner tube or on the inner wall of the outer burner tube. 15
8. A flame ionisation detector according to any of the preceding claims wherein said two burner tubes are mounted on a manifold having an inlet each for the combustible gas, for the 20 gas supporting combustion, for the column effluent and for make-up carrier gas. 20
9. A flame ionisation detector according to any of the preceding claims including means for connection to a supply of cooling gas to cool the ion-collecting electrode.
10. A flame ionisation detector according to any of the preceding claims wherein said two burner tubes are respectively connected to supplies of oxygen and hydrogen.
- 25 11. A method of operating a gas chromatograph having a flame ionisation detector according to any of the preceding claims wherein said flame ionisation detector is operated under conditions such that the response of said detector is 25
- (a) substantially proportional to the molar amount of an eluting organic solute;
- (b) substantially proportional to the weight of an eluting organic solute; or
- 30 (c) selective in favour of organic compounds containing elements other than carbon and hydrogen; 30
- and using said chromatograph to separate a mixture of organic compounds.
12. A flame ionisation detector according to claim 1, substantially as described hererin.
13. A flame ionisation detector substantially as illustrated in Fig. 1 of the accompanying 35 drawings. 35
14. A flame ionisation detector having a burner assembly substantially as illustrated in Fig. 2 of the accompanying drawings.
15. A flame ionisation detector having a burner assembly substantially as illustrated in Fig. 3 of the accompanying drawings.
16. The method of claim 11, substantially as described herein.

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ABSTRACT:

A flame ionisation detector comprises a burner 2 having two coaxial tubes 8 and 9, one for conveying to the flame a mixture of a first gas, eg. H₂, and the sample to be detected and the other for conveying to said flame a second gas, eg. O₂ which combusts with said first gas. The coaxial tubes 8, 9 can be of metal, eg. stainless steel, or ceramic, eg. alumina, magnesia, silica or zirconia. A polarising electrode 14 may be disposed in the burner 2, eg. formed as a wire 14 in inner tube 8, as shown, of Pt, W or stainless steel or as a metallic coating on a wall of one of the tubes 8, 9 formed by pyrolysis of tungsten or titanium halide. Preferably the sample is entrained in an inert carrier gas, eg. N₂ or He. The detector exhibits reduced levels of noise and standing current when supplied with oxygen and hydrogen and the response of the detector in a gas chromatograph can be manipulated by varying the flow rates

and proportions of the gases fed to the flame, whereby it is made to be responsive to the molar amount or the weight of an organic eluting solute or to be selective in favour of organic compounds containing elements other than carbon and hydrogen. <IMAGE>